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Structure and electrochemical properties of C_xF and $C_x(VF_5)_yF$ graphite intercalation compounds

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Abstract

Fluorine–graphite intercalation compounds, C_xF, and vanadium fluoride–graphite intercalation compounds, $C_x(VF_5)_yF$, have been prepared and characterized by X-ray powder diffraction (Debye–Scherrer method) and FT-IR spectroscopy. The reduction of these stage 1 and stage 2 compounds was carried out in a solution of $LiClO_4$ in propylene carbonate using the carbon paste electrode technique. It was observed that the potential of the reduction peak corresponding to the C_xF samples decreased with increasing values of x. For VF_5-containing compounds, three reduction peaks were observed, related to the reactions: $V^{V} \rightarrow V^{III}$, $V^{III} \rightarrow V^{0}$ and $F \rightarrow F^{-}$.

Introduction

The reaction of fluorine with graphite at low temperatures (<100 °C) in the presence of a suitable catalyst leads to the synthesis of fluorine–graphite intercalation compounds (GICs), denoted as C_xF [1, 2].

The intercalation of fluorine into the graphite lattice leads to the formation of 'nearly ionic bonds' or 'semi-ionic bonds' [1–6] with sp^2-hybridized carbon atoms. Traces of catalyst molecules are sometimes present in the lattices of the GICs. The preparation and electrochemical behaviour of such compounds has been reported in the literature [7–9].

Some GICs show higher electrical conductivity than the initial graphite. Since graphite fluorides used as cathodic materials in lithium primary batteries exhibit poor electrical conductivity, graphite intercalation compounds have been proposed recently as a substitute material [8, 9].

In this paper we present the method of preparation, the structural features (deduced from X-ray data) and the electrochemical behaviour of two kinds of GICs: C_xF and $C_x(VF_5)_yF$. For these latter compounds, FT-IR spectra were used for the determination of the nature of the intercalated species.

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Experimental

Preparation of $C_x(VF_5)_yF$ and C_xF samples

Vanadium fluoride GICs, $C_x(VF_5)_yF$, were prepared in a fluorine atmosphere using (a) natural graphite powder (57–74 μm) (see Table 1) or (b) Highly Oriented Pyrolytic Graphite (HOPG) (see Table 2).

A nickel vessel containing vanadium metal was placed at the bottom of a vertical nickel reactor. Several nickel vessels containing graphite were then set above the vessel containing vanadium. The temperature of the latter was gradually increased to 200 °C under vacuum. Under these conditions, the temperature of the graphite hosts was maintained between 100 °C and 180 °C. High purity fluorine gas supplied by Daikin Kogyo Company (purity: F_2, 99.4–99.7%; N_2, 0.3–0.6%; HF, <0.01%) was then introduced into the reactor at a pressure of 1 atm. Metallic vanadium reacts exothermically with fluorine gas giving VF_5, which is readily intercalated into the graphite together with fluorine. After 2–4 d, the $C_x(VF_5)_yF$ samples reported in Table 1 were obtained.

Fluorine–graphite intercalation compounds, C_xF, were prepared in a fluorine atmosphere containing 0.2–26% HF at room temperature (see Table 3). The host material was natural graphite powder (57–74 μm). The reaction was conducted for 1–3 weeks in most cases.

TABLE 1

Composition and X-ray data for $C_x(VF_5)F$ compounds prepared from natural graphite powder

Sample	Stage[a]	$I_c(c_0)$ (Å)	d_i[b] (Å)	a_0 (Å)
$C_{22.2}(VF_5)F$	(1)	8.260	4.906	2.454
	2	11.234	4.526	
$C_{20.7}(VF_5)F$	(1*)	8.794	5.440	2.447
	(1)	8.100	4.746	
	2	11.202	4.494	
$C_{16.9}(VF_5)F$	(1*)	8.902	5.548	2.450
	2	11.250	4.542	
$C_{12.4}(VF_5)F$	1*	8.582	5.228	2.454
	1**	14.438	–	
$C_{12.4}(VF_5)F$	1*	8.720	5.366	2.453
	1**	14.592	–	
$C_{10.3}(VF_5)F$	1*	8.858	5.504	2.454
	1**	14.183	–	

[a] ( ) = minor phase; 1* = stage 1 phase with large d_i value; 1** = stage 1 bi-intercalation phase.
[b] d_i (Å) = $I_c - 3.354n$ (n = stage number; 3.354 Å corresponds to the thickness of one carbon sheet).

TABLE 2

Composition of $C_x(VF_5)F$ samples prepared from HOPG; IR and X-ray diffraction data

Sample	Stage[a]	$I_c(c_0)$ (Å)	d_i[b] (Å)	Wavenumber[c] (cm^{-1})
$C_{22.0}(VF_5)F$	2	11.134	4.426	1581 (s); 785 (w)
$C_{17.3}(VF_5)F$	2	11.132	4.424	1584 (s); 795 (w)
$C_{16.7}(VF_5)F$	2*	11.693	4.985	1584 (s); 840 (vs)
$C_{14.8}(VF_5)F$	2	11.361	4.653	1578 (w); 780 (s)
$C_{13.5}(VF_5)F$	2*	11.803	5.095	1584 (m); 840 (m)
$C_{11.6}(VF_5)F$	1*	8.586	5.232	1584 (m); 840 (m)
	2*	11.732	5.024	
$C_{11.1}(VF_5)F$	1*	8.490	5.136	1590 (m); 840 (m); 785 (w)
	1	8.290	4.936	
$C_{10.7}(VF_5)F$	1*	8.511	5.157	1584 (m); 840 (s)
	2*	11.788	5.080	

[a] 1*, 2* = stage 1 or 2 phase with large d_i value.

[b] d_i (Å) = $I_c - 3.354n$ (n = stage number; 3.354 Å corresponds to the thickness of one carbon sheet).

[c] s = strong; m = medium; w = weak; v = very.

TABLE 3

Preparation mode, composition and X-ray data for C_xF samples prepared from natural graphite powder

Sample	Preparation mode		X-Ray data		
	HF (%)	Time (d)	Stage[a]	$I_c(c_0)$ (Å)	a_0 (Å)
$C_{6.1}F$	0.30	120	2	8.594	4.897
$C_{6.0}F$	0.25	18	2	9.096	4.912
$C_{5.1}F$	26.00	9	2	–	–
$C_{3.9}F$	0.40	14	1	10.748	2.456
			(2)	8.382	
$C_{3.0}F$	13.00	17	1	11.280	2.455
			(2)	8.336	
$C_{2.9}F$	3.00	25	1	11.388	2.447
			(2)	8.336	

[a] ( ) = minor phase.

Analysis of the products

The GICs were analyzed using a Shimadzu XD-610 X-ray diffractometer. Their stage number was determined from the repeat distance along the c-axis (I_c value) which was calculated from the (00l) diffraction lines. Powder samples were also analyzed by the Debye–Scherrer method. In addition, the samples containing vanadium fluoride were subjected to FT-IR spectroscopy using a Nicolet 200 XB FT-IR spectrometer. As described in a previous paper [10], the $C_x(VF_5)_yF$ samples prepared under the above experimental conditions usually have the composition $C_x(VF_5)F$ (i.e. $y=1$). Hence, in this work, the composition of all the GICs was calculated from the weight increase and $y=1$ was postulated for the vanadium fluoride GICs.

Electrochemical experiments

Experiments were carried out at 25 °C in a polypropylene cell, as described in ref. 11. As previously reported, the carbon paste electrode technique was used. The working electrode was a mixture of GIC (<0.025 g) and 'Ultra-F' purity graphite Johnson Matthey, Ultra Carbon, conducting grade, 100 mesh (0.10 g) wetted with a few drops of electrolyte. The latter was a molar solution of lithium perchlorate (purum Fluka) in propylene carbonate (PC) for synthesis (Merck).

Two kinds of reference electrode have been prepared:

(i) Ag/AgI system: silver wire, coated with a layer of silver iodide, immersed in a 0.1 M solution of sodium iodide in PC. The electrode was separated from the main compartment of the cell by means of a PVDF junction [11, 12]. Its potential was +2.60 V versus a lithium reference electrode (lithium rod in a 1 M $LiClO_4$ solution).

(ii) I_2/I^- system: platinum wire, immersed in an I_2 (0.05 M)/I^- (0.10 M NaI) solution in PC. The electrode was separated from the main compartment of the cell by a glass frit. Its potential was +3.05 V versus a lithium reference electrode.

All the data hereafter refer to the Ag/AgI system to allow ready comparison with results obtained previously [7].

A platinum auxiliary electrode was used as described previously [7, 11]. A slow potential scan (rate $=0.02$ mV s^{-1}) was imposed on the working electrode by means of a PAR 273 potentiostat.

Results and discussion

Composition and stage number of the GICs

C_xF compounds

The composition, stage number and X-ray data are shown in Table 3, in which the $C_{6.1}F$ to $C_{5.1}F$ samples are stage 2 compounds and the $C_{3.9}F$ to $C_{2.9}F$ samples are quasi-stage 1 compounds containing small amounts of stage 2 phases. Tables 4 and 5 present examples of indexed results for quasi-stage 1 and stage 2 compounds. The diffraction line, No. 1, in Table 4 was indexed as (002) because stage 1 C_xF has a large I_c value between 10.5 Å and 12 Å when a small amount of a volatile fluoride such as HF, SbF_5 or WF_6 is used as the catalyst for fluorine intercalation. In this case, the fluorine intercalation rate is not high [6]. This is due to the alternate

TABLE 4

X-Ray powder diffraction data for stage 1 + (2)[a] $C_{2.9}F$ compounds

No.	Intensity[b]	$1/d^2$ (obsd.) ($Å^{-2}$)	$1/d^2$ (calcd.) ($Å^{-2}$)	*hkl*	Stage
1	vs	0.0308	0.0308	002	1
2	m, vbr	0.0576	0.0576	002	2
3	vs	0.2231	0.2227	100	–
4	s	0.6675	0.6675	110	–
5	vw	0.8900	0.8908	200	–
6	vw	1.5586	1.5589	210	–

[a] ( ) = minor phase.

[b] s = strong; m = medium; w = weak; v = very; br = broad.

Hexagonal lattice: $c_0 = 11.388$ Å (stage 1), 8.336 Å (stage 2); $a_0 = 2.447$ Å.

TABLE 5

X-Ray powder diffraction data of stage 2 $C_{6.0}F$ compounds

No.	Intensity[a]	$1/d^2$ (obsd.) ($Å^{-2}$)	$1/d^2$ (calcd.) ($Å^{-2}$)	*hkl*
1	s	0.0483	0.0483	002
2	vw	0.0552	0.0553	100
3	w	0.1652	0.1658	110
4	s	0.2225	0.2212	200
5	w, br	0.2391	0.2333	201
6	s	0.6621	0.6632	220
7	vw, br	0.7121	0.7115	222

[a] s = strong; w = weak; v = very; br = broad.

Hexagonal lattice: $c_0 = 9.096$ Å; $a_0 = 4.912$ Å.

insertion of ionically and semi-ionically bonded fluorines between the carbon sheets.

The (002) diffraction lines for stage 2 phases in quasi-stage 1 compounds are all very broad and not strong. The I_c values for these stage 2 phases are approximately 8.3–8.4 Å, indicating that the thickness of the intercalated species is 1.6–1.7 Å. This means that even in the stage 2 phases fluorine has a semi-ionic bond with the carbon atoms [6]. As only very sharp (*h*00) and (*hk*0) lines were observed in most cases, except for the (002) diffraction lines, the stacking of the carbon sheets would seem to be somewhat disordered. The lattice parameter, a_0, was in the range 2.456–2.447 Å. Its value decreased with increasing fluorine intercalation.

A superlattice with the lattice parameter $a_0 = 2a_g$ was observed at stage 2 (a_g is the lattice parameter for graphite). This indicates that the intercalated fluorines are orientated with a high regularity between the carbon sheets as reported previously [6]. The existence of only one strong (002) diffraction line and an I_c value of 9.1 Å which is slightly less than 9.4 Å shows that the intercalated fluorines have some covalency with the carbon atoms. Hence, the fluorine species are not orientated at the centre of two carbon sheets, but their position is slightly deviated alternately upwards or downwards from the centre. The low values of a_0 and I_c obtained with $C_{6.1}F$ suggest that strong C—F bonds are present in this compound.

$C_x(VF_5)F$ *compounds*

The composition and X-ray data for $C_x(VF_5)F$ samples prepared with natural graphite are given in Table 1. Samples $C_{22.2}(VF_5)F$ to $C_{16.9}(VF_5)F$ are stage 2 compounds containing small amounts of stage 1 phases; $C_{12.4}(VF_5)F$ and $C_{10.3}(VF_5)F$ are stage 1 compounds. In stage 2 phases of the samples $C_{22.2}(VF_5)F$ to $C_{16.9}(VF_5)F$, the sizes of the intercalated species, d_i, were *c.* 4.5 Å. These values are lower than those for the VF_6 and VF_5 species, i.e. 4.8 Å and 4.9 Å, respectively [10]. Thus, it is thought that six fluorine atoms of the intercalated VF_6 octahedra nestle in the hexagons of the carbon sheets (nestling of VF_6). The nestling of the hexafluoro anion into hexagons of the carbon sheets reduces the apparent separation between two carbon sheets by 0.2–0.6 Å [10].

Stage 1 phases have different d_i values (4.7–4.9 Å and 5.2–5.5 Å) and large I_c values (14.2–14.6 Å). The two former large d_i values were observed in stage 1 phases contained in stage 2 compounds of the type $C_{22.2}(VF_5)F$ to $C_{16.9}(VF_5)F$, and the two latter values were found in highly concentrated stage 1 compounds of the type $C_{12.4}(VF_5)F$ and $C_{10.3}(VF_5)F$. Phases having d_i values equal to 4.7–4.9 Å may be those in which non-nestling VF_6 species are intercalated as suggested by the IR spectra. However, the phases with d_i values of 5.2–5.5 Å could be assigned to those where VF_5 and excess fluorine are co-intercalated as reported in a previous paper [13]. It is shown later via IR spectral data that VF_5 molecules are intercalated with excess fluorine in a phase having a large d_i value equal to or greater than 5 Å. Co-intercalation of fluorine can increase the apparent size of the intercalated species to a value greater than that of the VF_5 molecule, i.e. 4.9 Å.

Phases with large I_c values (14.2–14.6 Å) have been interpreted in terms of a bi-intercalation phase consisting of a fluorine-intercalated layer (5.7 Å including the thickness of one carbon sheet) and a VF_5 + excess fluorine intercalated layer (8.5–8.9 Å including the thickness of one carbon sheet) [13]. For this reason, stage 1 compounds may contain a greater excess of fluorine atoms than VF_6.

The lattice parameter, a_0, was approximately 2.45 Å in all the samples. It is smaller than that in pristine graphite ($a_g = 2.462$ Å) due to charge transfer from carbon to the intercalated fluorine and vanadium fluoride.

Tables 6 and 7 present examples of X-ray powder diffraction data. In each case, few (00*l*) and (*hkl*) diffraction lines were observed. This means that the intercalated vanadium fluoride and fluorine do not have a regular orientation between the carbon sheets. Furthermore, all the (00*l*) diffraction lines are very broad in the stage 1 compounds $C_{12.4}(VF_5)F$ and $C_{10.3}(VF_5)F$, while they are sharp in the stage 2 phase-dominant compounds $C_{22.2}(VF_5)F$

TABLE 6

X-Ray powder diffraction data for stage 2+(1)[a] $C_{22.2}(VF_5)F$ compounds

No.	Intensity[b]	$1/d^2$ (obsd.) ($Å^{-2}$)	$1/d^2$ (calcd.) ($Å^{-2}$)	*hkl*	Stage
1	m	0.0586	0.0586	002	1
2	s	0.0726	0.0711	003	2
3	w	0.1246	0.1264	004	2
4	w	0.2215	0.2215	100	–
5	w, br	0.2387	0.2362	101	1
6	w	0.6642	0.6642	110	–

[a]( ) = minor phase.

[b]s = strong; m = medium; w = weak; br = broad.

Hexagonal lattice: $c_0 = 11.234$ Å (stage 2), 8.260 Å (stage 1); $a_0 = 2.454$ Å.

TABLE 7

X-Ray powder diffraction data for stage 1 $C_{12.4}(VF_5)F$ compounds

No.	Intensity[a]	$1/d^2$ (obsd.) ($Å^{-2}$)	$1/d^2$ (calcd.) ($Å^{-2}$)	*hkl*	Stage
1	m, vbr	0.0164	0.0188	002	1**
2	m, vbr	0.0526	0.0526	002	1*
3	w, vbr	0.0751	0.0752	004	1**
4	m	0.2215	0.2217	100	–
5	vw	0.6653	0.6642	110	–

[a]m = medium; w = weak; v = very; br = broad.

Hexagonal lattice: $c_0 = 8.720$ Å (stage 1*, phase with large d_i value), 14.592 Å (stage 1**, bi-intercalation phase); $a_0 = 2.453$ Å.

to $C_{16.9}(VF_5)F$. The breadth of the (00*l*) lines could arise from the co-intercalation of excess fluorine which increases the d_i value to greater than 5 Å.

Table 2 lists the IR absorption bands and X-ray data for stage 2 compounds and admixtures of stages 1 and 2 prepared with HOPG. The absorption band observed at *c.* 1584 cm^{-1} is due to the vibration of the graphite lattice. Compounds having 5 Å or more as d_i values possess an absorption band at 840 cm^{-1}. However, those with d_i values of 4.9 Å or less exhibit absorption bands at *c.* 785 cm^{-1}. Although VF_5 gas exhibits a strong absorption at 800 cm^{-1} [14], its absorption band is generally shifted to some extent when the VF_5 molecule is accommodated between two carbon sheets. For GICs prepared with MF_5, MF_6^- and MF_7^{2-} (M = Nb, Ta), the wavenumber $\bar{\nu}$ of the absorption band characteristic of intercalated fluoride may be compared with that of gaseous VF_5 [15, 16]: $\bar{\nu}(C_xMF_7) < \bar{\nu}(C_xMF_6) < \bar{\nu}(\text{gaseous } MF_5) < \bar{\nu}(C_xMF_5)$.

From the similarity between the shifts in the absorption bands in our GICs, that observed at 840 cm^{-1} may be assigned to VF_5 molecules and those at *c.* 785 cm^{-1} to VF_6^- anions. Since the smaller d_i values (< 4.8 Å) are ascribed to the nestling of the VF_6^- anions into the hexagons of the carbon sheets [10], the above assignment is in good agreement with the X-ray diffraction data.

IR spectra and X-ray data thus indicate that intercalated VF_6 is dissociated into VF_5 and fluorine in highly concentrated and low-stage compounds, while VF_6^- anions nestle into the hexagons of the carbon sheets in low concentration samples or higher stage compounds. The VF_6 octahedra may therefore be less stable than NbF_6 or TaF_6 octahedra. A stronger repulsion force would operate among the fluorine atoms in VF_6 than in NbF_6 or TaF_6 because of the smaller size of the vanadium cations compared to that of niobium or tantalum cations. This would be the main reason why VF_6^- is dissociated into a VF_5 molecule and excess fluorine in highly concentrated compounds. Furthermore, the carbon sheets are not easily adjusted in the highly concentrated state so that the VF_6^- anion could nestle in the hexagons of the carbon sheets.

Electrochemical behaviour

C_xF compounds

One or two reduction peaks were observed with all the samples. The potential corresponding to the maximum of the current intensity increases with increasing fluorine content of the samples (see Table 8). This means that reduction of the compounds becomes more and more difficult with decreasing fluorine content.

The potential of the reduction peak for commercial grade graphite fluorides, $CF_{1.1}$ and $CF_{0.65}$, with covalent bonds between the carbon and fluorine, was found to lie in the -0.2 to -0.75 V potential range [7, 11]. Thus, depending on the stoichiometric factor x, the GIC may be easier or more difficult to reduce than the graphite fluoride sample CF_x.

The C_xF GICs contain ionic or semi-ionic C—F bonds. It is thought that reduction may be easier for the GICs relative to the graphite fluorides only if the fluorine atoms, as well as the solvated lithium cations, can diffuse between the carbon sheets (mutual diffusion). This is only possible if the interlayer distance is sufficiently large. In the case of CF_x compounds, only

TABLE 8

Electrochemical behaviour of C_xF compounds. Experimental (Q_{exp}) and theoretical (Q_t) charge for complete reduction; potential (E) of peak(s)

x	m (mg)	E (V)	Q_{exp} (C)	Q_t (C)
6.1	20.0	−1.60	21.0	21.2
6.0	7.4	−1.26	7.0	7.9
5.1	17.0	−0.58 and 0	18.0	20.3
3.9	12.0	−0.50	14.5	17.0
2.9	10.0	−0.15 and +0.10	5.5	18.3

solvated Li^+ cations diffuse into the lattice because the C−F bonds are covalent.

It was observed that the two samples $C_{5.1}F$ and $C_{2.9}F$ prepared with larger amounts of HF exhibit two reduction peaks. This may be attributed to the reduction of two kinds of fluorine species: solvated with HF or unsolvated.

Except for the first sample $C_{2.9}F$, the total quantity of electricity Q_{exp} necessary for complete reduction of the compound, as calculated from the peak areas, is in good agreement with the expected theoretical value Q_t (see Table 8).

$C_x(VF_5)F$ *compounds*

The compounds prepared with natural graphite were subjected to electrochemical experiments. The voltammograms obtained exhibit two peaks at −0.15 V (peak No. 1) and −1.50 V (peak No. 2) versus Ag/AgI, and a third peak (peak No. 3) whose position depends strongly on the stoichiometric coefficient x, as shown in Fig. 1. Although deconvolution of the peaks is not easy, it is clear that, as in the case of the C_xF compounds reported above, the potential of peak No. 3 decreases for increasing values of x.

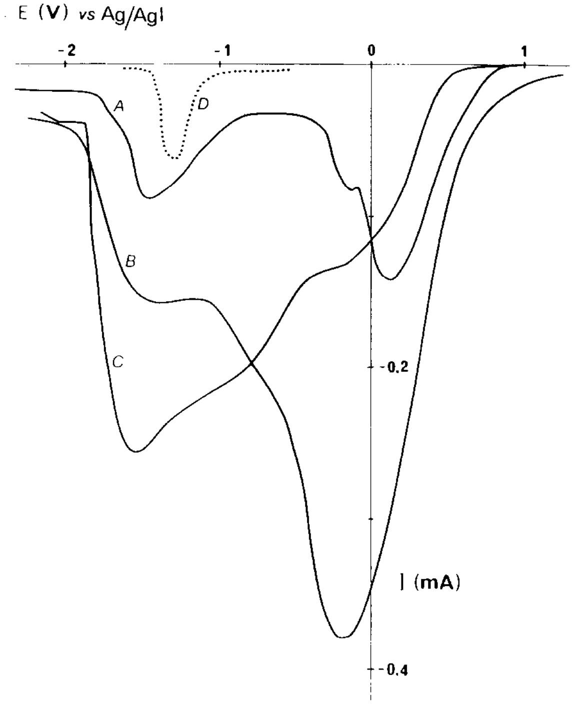

Fig. 1. Electrochemical behaviours as demonstrated by linear sweep voltammetry: rate = 0.02 mV s^{-1}; reference electrode Ag/AgI. $C_x(VF_5)F$ GICs: $x = 12.4$ (curve A); $x = 16.9$ (curve B); $x = 20.7$ (curve C). VF_3: curve D.

TABLE 9

Electrochemical behaviour of $C_x(VF_5)F$ compounds. Experimental (Q_{exp}) and theoretical (Q_t) charge for complete reduction

x	m (mg)	Q_{exp} (C)	Q_t (C)
22.2	21.30	18.0	22.6
20.7	20.00	16.0	28.0
16.9	20.00	21.0	31.3
12.4	3.50	6.4	6.5
10.3	4.25	8.6	8.5

However, for the first compound ($x = 10$), peak No. 3 is hidden by peak No. 1 which appears at approximately the same potential.

These results suggest that reduction of both the C_xF and the intercalated VF_5 occurs. It is thought that peaks Nos. 1 and 2 are related to the reduction of the vanadium species because they appear roughly at the same potential for each sample. As VF_5 and VF_3 are reported to be the most stable vanadium fluorides [17], peak No. 1 would correspond to the reduction $V^V \rightarrow V^{III}$ and peak No. 2 to $V^{III} \rightarrow V^0$.

Another experiment was necessary to determine the reduction potential of pure VF_3 under the same experimental conditions. For this purpose, VF_3 samples (yellow–green powders) were prepared by direct fluorination of vanadium metal in a fluorine atmosphere. The purity of the samples was ascertained by X-ray diffraction. As shown in Fig. 1, reduction of VF_3 occurs at -1.3 V. The reduction yield is low (1.4%). The reduction potential of pure VF_3 must be higher than that of the VF_3 species trapped in the carbon lattice. Hence, this result is consistent with our attribution of peak No. 2 to the reduction of VF_3.

In contrast, peak No. 3 would be related to the reduction of the intercalated fluorine, as in the case of the C_xF compounds.

For most experiments, the total quantity of electricity Q_{exp} necessary for complete reduction of the $C_x(VF_5)F$ compounds, calculated from the peak areas, was in good agreement with the expected theoretical value Q_t (see Table 9).

In conclusion, the electrochemical behaviour of the C_xF GICs depends strongly on their stoichiometric coefficient x and on their mode of preparation (amount of HF in the gas phase). When vanadium fluoride is intercalated, the reduction process includes the reduction of this fluoride and of excess fluorine.

References

1 T. Nakajima and N. Watanabe, *Graphite Fluorides and Carbon–Fluorine Compounds*, CRC Press, Boca Raton, FL, 1991, p. 123.

2 N. Watanabe, T. Nakajima and H. Touhara, *Graphite Fluorides*, Elsevier, Amsterdam, 1988, p. 240.
3 I. Palchan, M. Crespin, H. Estrade-Szwarckopf and B. Rousseau, *Chem. Phys. Lett.*, *157* (1989) 321.
4 R. Hagiwara, M. Lerner and N. Bartlett, *J. Chem. Soc., Chem. Commun.*, (1989) 573.
5 D. Vaknin, I. Palchan, D. Davidov, H. Selig and D. Moses, *Synth. Metal.*, *16* (1986) 349.
6 T. Nakajima, M. Molinier and M. Motoyama, *Carbon*, *29* (1991) 429.
7 T. Nakajima, D. Devilliers and M. Chemla, *J. Fluorine Chem.*, *46* (1990) 461.
8 R. Hagiwara, M. Lerner, N. Bartlett and T. Nakajima, *J. Electrochem. Soc.*, *135* (1988) 2393.
9 A. Hamwi, M. Daoud and J. C. Cousseins, *Synth. Metal.*, *30* (1989) 23.
10 T. Nakajima, T. Matsui, M. Motoyama and Y. Mizutani, *Carbon*, *26* (1988) 831.
11 D. Devilliers, B. Teisseyre, M. Chemla, N. Watanabe and T. Nakajima, *J. Fluorine Chem.*, *40* (1988) 1.
12 H. J. MacComsey Jr. and M. S. Spritzer, *Anal. Lett.*, *3* (1970) 427.
13 T. Nakajima and T. Matsui, *Tanso*, *145* (1990) 273.
14 H. H. Claassen and H. Selig, *J. Chem. Phys.*, *44* (1966) 4039.
15 A. Hamwi and Ph. Touzain, *Rev. Chim. Miner.*, *19* (1982) 432.
16 S. Mouras, A. Hamwi, D. Djurado and J. C. Cousseins, *Rev. Chim. Miner.*, *24* (1987) 572.
17 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1984.